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ABSTRACT: This work presents a comprehensive study on fast, low-cost methods for the electronic passivation of the phosphorus-diffused front surface and the non-diffused *p*-type rear surface of crystalline Si solar cells. Titanium dioxide is compared with rapidly-grown thermal oxide (RTO) and PECVD silicon nitrides from three different laboratories. Double layers of RTO and TiO₂ or SiN are also investigated. We demonstrate that SiN and RTO single layers can provide very good passivation on both the front and back surface of solar cells. It is also shown that double layers consisting of a thin RTO film and silicon nitride can improve the passivation quality of most SiN layers, and enhance the stability under thermal treatment. With the proper choice of RTO, SiN, and thermal treatment, excellent surface recombination velocities on the back as well as very low emitter saturation currents can be reached using these fast, industrially feasible methods. All films used also provide or are compatible with a good antireflection coating of the cell surface.

Keywords: c-Si − 1: Passivation − 2: Silicon-Nitride − 3

1. INTRODUCTION

The objective of this work is to provide a comprehensive and systematic investigation of front and back surface passivation schemes for laboratory and industrial (screen-printed) Si solar cells. For industrial cells, titanium dioxide (TiO₂) is widely used as an antireflection (AR) coating on the front. On the back of these devices, either no passivation or an Al back surface field (BSF) is used. In contrast, on laboratory solar cells a variety of different passivation schemes, including conventional furnace oxides (CFOs) grown at high temperature, provide low recombination on both the front and the back surface.

This investigation tries to bridge the gap between these two approaches by providing fast, low-cost methods for effective surface passivation. As an alternative to CFO, which requires lengthy high-temperature processing, rapid thermal oxides (RTO) can give comparable passivation in a much shorter time. Additionally, plasma deposition (PECVD) of silicon nitride (SiN) has emerged as a lowtemperature passivation method, which simultaneously provides good antireflection properties. These low-cost methods can provide effective surface passivation in a short time and with a much lower thermal budget than a CFO, while still providing good AR properties. Their effectiveness for solar cell passivation has been demonstrated previously [1, 2]. In this work, we compare the quality of TiO₂, RTO, and plasma-deposited SiN for emitter and back surface passivation. Double layers of thin (< 10 nm) silicon oxide and SiN or titanium dioxide are also considered. The effects of emitter sheet resistance, surface texture, and different SiN depositions are investigated for all of these schemes. The impact of post-growth/post-deposition treatments such as a forming gas anneal (FGA) and the firing of screen-printed contacts is examined. Silicon nitrides from three different laboratories are compared to account for the considerable variability in the deposition parameters

connected with this technique. We compare two different direct-plasma nitrides from parallel-plate reactors with one microwave-excited remote SiN, which has been shown to give excellent surface passivation on low-resistivity *p*-type silicon wafers [2,3]. These nitrides differ primarily in the mode of plasma excitation and the deposition temperature, which was 300°C and 350°C for the two direct SiN films and 400°C for the remote SiN.

2. EXPERIMENTS

For the investigation of the surface passivation on ptype material we used 1.3-Ωcm <100> FZ silicon wafers, whereas the investigation of the emitter passivation was performed on phosphorus-diffused high-resistivity (750 Ω cm) FZ *n*-Si wafers. We studied emitters with sheet resistances of 40 Ω/\Box and 90 Ω/\Box , which are suitable for screen-printed or evaporated contacts, respectively. Some of the wafers were subjected to a chemical random surface texturing before processing. Samples for the emitter passivation experiments were diffused on both sides in a rapid thermal processing (RTP) system using a phosphorus spin-on dopant source. After removal of the phosphosilicate glass, some of the diffused and the non-diffused samples were oxidized in the same RTP system used for the diffusions. This rapid thermal oxidation at 900°C for 150 s resulted in an oxide thickness of ~6 nm. The oxidized non-diffused samples were then annealed in forming gas at 400°C for 15 min. Subsequently, depositions of passivating films were performed in three different laboratories. The thickness of these films was approximately that of a single-layer AR coating. The refractive indices of these films were between 2.15 and 2.27 at $\lambda = 632.8$ nm, which is close to the optimum for a single-layer AR coating under glass or the first film of a double-layer AR coating in air [4].

The deposition of TiO_2 was performed by evaporating titanium in an oxygen atmosphere at a low pressure of 15 mPa. For the deposition of SiN, three different PECVD systems were used. Two of these systems are parallel-plate reactors with high-frequency excitation and deposition temperatures of 300°C and 350°C, respectively. The third system is a remote PECVD system with microwave excitation and a deposition temperature of $400^{\circ}C$ [5]. Table 1 summarizes the differences in the key parameters of these systems.

Note that the deposition temperature has a strong impact on the passivation quality of the SiN film. Temperatures around 400°C usually result in the best passivation for both plasma excitation methods [6]. The plasma deposition systems vary in a number of other aspects, such as the reactor geometry, the plasma power and the pressure. However, all three SiN films are used as a standard in the respective laboratories.

Table 1: Plasma depositions used in this work.

Film No.	Excitation mode	Deposition temperature	Gases
SiN_1	direct, HF (13.6 MHz)	300°C	SiH ₄ , N ₂ , NH ₃
SiN_2	direct, HF (13.6 MHz)	350°C	SiH ₄ (5%) in He, N ₂ , NH ₃
SiN_3	remote, 2.45 GHz	400°C	SiH ₄ , NH ₃

After the film deposition, the effective carrier lifetime $\tau_{\rm eff}$ was measured at room temperature on every sample. Subsequently, a forming gas anneal (FGA) at 400°C was performed on all samples. As a final step, the samples were subjected to a short temperature cycle with a maximum temperature of 730°C, which is typically used as a firing cycle for screen-printed contacts. This step was performed in a beltline furnace with infrared heating.

The effective carrier lifetime $\tau_{\rm eff}$ was measured after each step using a commercially available inductively-coupled PCD tester [7]. From these $\tau_{\rm eff}$ data, the emitter saturation current density $J_{0\rm e}$ (for diffused samples) or the effective surface recombination velocity $S_{\rm eff}$ was calculated. $J_{0\rm e}$ was calculated from the injection level dependence of the inverse effective lifetime (minus the Auger recombination rate) under high-injection conditions [8]. For this calculation we used a linear fit in the injection level range 1×10^{14} cm⁻³ to 2×10^{15} cm⁻³. For the calculation of $S_{\rm eff}$ an infinite bulk lifetime $\tau_{\rm b}$ was assumed, and hence the resulting quantity is denoted $S_{\rm eff,max}$. It is important to note that these PCD measurents do not represent the exact condition of a solar cell because the effect of contact recombination is neglected.

3. RESULTS AND DISCUSSION

3.1 Passivation of screen-printable emitters

The passivation of solar cell front surfaces was investigated on both 40- Ω/\Box and 90- Ω/\Box emitters. On 40- Ω/\Box emitters (which can accommodate screen-printed contacts) the surface is largely decoupled from the bulk,

because of the high surface dopant concentration and the large depth of the doping profile. Despite this, high-quality RTO or SiN_3 passivation was able to reduce J_{0e} by a factor of 2-3 compared with TiO₂, which offered virtually no measure of passivation (see Figure 1). SiN_1 (deposited at 300°C) is clearly inferior to RTO or SiN_3. The combination of RTO and SiN_3 results in the best emitter passivation (174 fA/cm² on planar samples). Note that the high-temperature RTO treatment slightly changes the doping profile (reduced surface dopant concentration, increased emitter thickness), facilitating the achievement of a good surface passivation. The J_{0e} values of textured samples are about 1.5 to 2 times higher than those of planar ones, which resembles the increase in surface area.

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Figure 1: Measured emitter saturation current densities of different passivation schemes on $40-\Omega/\square$ emitters.

3.2 Passivation of 90- Ω/\Box emitters

On relatively transparent $90-\Omega/\square$ emitters, the difference in the degree of passivation for various schemes is more pronounced, as Figure 2 shows. Again, TiO₂ does not provide any significant reduction of J_{0e} . For the planar surface, RTO growth reduces J_{0e} by more than a factor of 10 to below 100 fA/cm^2 , as does the deposition of SiN_3. However, on the textured surface RTO alone is not as effective, resulting in a moderate J_{0e} value of 400 fA/cm^2 . Here, SiN_3 is clearly superior.

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Figure 2: Measured emitter saturation current densities of different passivation schemes on $90-\Omega/\square$ emitters.

Double layers of RTO and SiN were better than the nitrides alone in all cases, resulting in very low $J_{0\rm e}$ values of less than 50 fA/cm² for planar and 100 fA/cm² for textured emitter surfaces (see Figure 2). A 400°C forming gas anneal does not change the surface passivation appreciably. The same applies for the contact firing cycle on the 40- Ω / \square emitters. For comparison, thin furnace oxides (CFOs) were grown on the same emitters. This passivation resulted in identical or only negligibly lower $J_{0\rm e}$ values than the RTO.

3.3 Back surface passivation

On $1.3-\Omega$ cm p-Si wafers (see Figure 3), the deposition of TiO_2 does not give any measurable surface passivation, nor does the growth of RTO or the deposition of SiN_1 . Note that S_{eff} values above 10^4 cm/s cannot be measured reliably by the method used in this study. As Figure 3 shows, the SiN_1 and RTO passivations both improve considerably after an FGA. While as-deposited SiN_3 already gives very good passivation (27 cm/s on planar surfaces), double layers of RTO with all nitrides result in excellent S_{eff} values after an FGA. The same trend is found for textured surfaces (Fig. 3b), with SiN_3 giving much better passivation than the other nitrides. After an FGA, all RTO/SiN double layers show good passivation, resulting in a low $S_{eff,max}$ value of 39 cm/s for RTO/SiN_3.

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Figure 3: Measured maximal S_{eff} values of different passivation schemes on (a) *planar* and (b) *textured* 1.3-Ωcm

p-Si wafers. S values above 10⁴ cm/s cannot be resolved by the measurement technique used and hence are not shown.

3.4 Thermal stability of passivation schemes

For most industrial processes these high-quality passivation schemes must withstand the heat treatment associated with the firing of screen-printed contacts. Therefore, the stability of the passivation schemes on 1.3-Ωcm p-Si was evaluated after a thermal cycle with a peak temperature of 730°C in a beltline furnace, simulating the contact firing. Figure 4 indicates that the SiN singlelayer passivation resulted in moderate to low $S_{\rm eff}$ values after this heat treatment, with SiN_1 and SiN_3 showing some degradation of $S_{\rm eff}$. Interestingly, the RTO/SiN double layers provided excellently low $S_{\rm eff}$ values, regardless of the type of silicon nitride used. After this heat treatment, the double layer with SiN_1 resulted in the lowest $S_{\rm eff,max}$ value (12 cm/s) observed in this work. Thus, not only can the RTO film enhance the stability of SiN films under thermal treatment, it even improves the surface passivation if subjected to this anneal. Also, the passivation quality of the RTO/SiN double-layers is nearly independent of which SiN film is used.

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Figure 4: Measured effective surface recombination velocities of planar 1.3- Ω cm *p*-Si wafers before and after 730°C annealing.

In principle, the back surface passivations mentioned above are also suitable for the passivation of the rear surface of bifacial solar cells. This application additionally requires a good UV stability of the passivation schemes [2]. Presently, we have only performed such a testing for the silicon nitride films SiN_3. As shown in Ref. 9 there is a slight UV degradation of the passivation quality of SiN_3 films, however, the degradation rate is so slow that it has negligible impact on the long-term stability of highly efficient bifacial cells. Bifacial cells fabricated at ISFH using the SiN_3 rear surface passivation have achieved excellent rear efficiencies above 18% [10].

4. IMPACT ON SOLAR CELL EFFICIENCY

To estimate the possible improvement of industrial solar cells, simulations were performed with the one-dimensional modeling program PC-1D. The simulated cells have a $40-\Omega/\square$ emitter, a grid shading of 6%, and a fill factor of 0.77 - 0.78 which is representative for high-quality screen-printed Si solar cells. The calculations show that high-efficiency industrial cells, which are 14-15% efficient today, can receive a gain of up to 0.9% (absolute) by improving the front surface passivation.

The effect of back surface passivation depends strongly on the cell thickness and the bulk lifetime. For example, a 300 μ m thick cell made on high-lifetime (200 μ s) material receives a boost of about 1.3% reaching an efficiency of 18%, provided the area-averaged $S_{\rm eff}$ at the back surface can be reduced below 100 cm/s. Such low values can indeed be achieved if the above-mentioned surface passivations (SiN_3 or RTO/SiN double layers) are combined with a local BSF below the rear contact grid

[10]. Optimized screen-printed BSFs alloyed by RTP have already demonstrated $S_{\rm eff}$ values as low as 200 cm/s [1,11].

For low-lifetime materials, the increase in the cell efficiency is still considerable. Table 2 summarizes the possible improvements for solar cells with 20 μ s or 200 μ s bulk lifetime and 300 μ m or 100 μ m wafer thickness, respectively. For TiO₂ on the front, we assumed a J_{0e} of 520 fA/cm², whereas we used 174 fA/cm² for the best (i.e., RTO + SiN_3) passivation of phosphorus-diffused emitters. On the back surface, we used an $S_{\rm eff}$ value of 10^4 cm/s for non-passivated and 100 cm/s for optimally passivated samples.

Table 2: Calculated efficiencies of Si solar cells without and with surface passivation on front and back (see text for details).

Bulk lifetime [µs]	Cell thickness [µm]	TiO ₂ on front	Best front passivation	Front and back passi- vation
200	300	15.9%	16.8%	18.1%
200	100	14.5%	16.2%	17.6%
20	300	15.4%	15.9%	16.6%
20	100	14.4%	14.9%	17.0%

The simulations show that with SiN_3 or RTO/SiN back surface passivation an efficiency of 17% can be reached even on a 100 μ m thin substrate with a bulk lifetime of only 20 μ s. Note that in this case the thinner substrate gives a higher efficiency than a 300 μ m thick wafer. Application of RTO/SiN passivation may result in considerable cost reduction of commercial PV cells, which are only about 11-14% efficient today.

5. CONCLUSIONS

This study provides a thorough investigation of solar cell surface passivation by RTO, TiO₂, and different PECVD silicon nitrides. The deposition or growth of these films can be performed in a matter of minutes, and all of these passivation schemes provide (or are compatible with) near-optimum antireflection properties. Thus, they can significantly enhance the performance of current industrial solar cells. We show that both a RTO film and different silicon nitrides can reduce the surface recombination substantially on both the emitter and rear surface of the cell.

Three PECVD SiN deposition systems, differing in various aspects, are used, and the variation in the resulting film passivation qualities is investigated. We find that this variation leads to considerable differences in the passivation of emitter surfaces, and to an even stronger contrast on non-diffused *p*-type silicon. Here, 400°C remote SiN is clearly outperforming the other nitrides investigated in this work.

It is demonstrated that double layers of RTO with SiN can improve the surface passivation even further, resulting in excellently low J_{0e} values below 50 fA/cm 2 on $90\text{-}\Omega/\square$ emitters, and S_{eff} values below 20 cm/s on a planar $1.3\text{-}\Omega\text{cm}$ Si surface. The combination of RTO and SiN can

also reduce the gap in passivation quality between the different nitrides. Furthermore, this combination is shown to enhance the stability of the surface passivation under thermal treatment such as firing of screen-printed contacts, and to provide excellently low back-surface $S_{\rm eff}$ values regardless of the type of SiN used. Therefore, appropriate cell design and thickness in conjunction with such effective passivation schemes on the front and back, can lead to low-cost solar cells with higher efficiency in the future. Application of high-quality RTO/SiN passivation in conjunction with an effective local BSF offers the possibility of 17%-efficient 100 μm thin commercial cells with effective bulk lifetimes as low as 20 μs .

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